

Chem 220a - Organic Chemistry

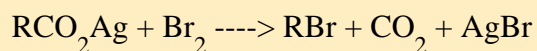
Problem Set 3

Chapter 4

Due: Monday, October 1, 2001

**Alexander Borodin (1833-1887)**

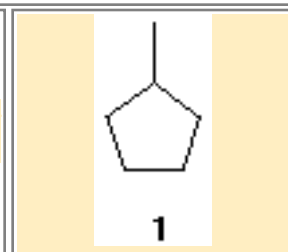
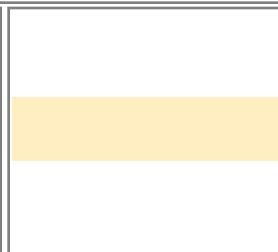
Besides being an accomplished composer and a member of the "Russian Five" (Cui, Mussorgsky, Rimsky-Korsakov, and Balakirev), Borodin was an accomplished organic chemistry. He studied the aldol condensation, determined urea in urine, and conducted studies on the decarboxylation of silver salts of carboxylic acid with bromine (1861).



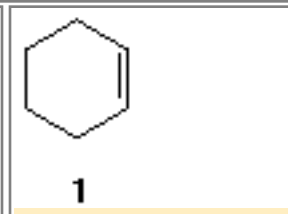
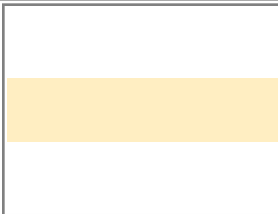
Although he did not identify the alkyl bromide, he was investigating a free radical reaction. It was not until the Hunsdieckers, Mann und Frau, for whom the process is named, recognized the full scope of the reaction in 1942.

1. Study the Alkane Module in [Organic Reactions Go Online](#) (ORGO).
2. The Hunsdiecker reaction forms an intermediate, thermally unstable compound **A** prior to the formation of products. Since silver bromide is formed along with **A**, the identity of **A** (think metathesis) should be readily apparent. Show the initiation, propagation and decarboxylation steps of this radical chain reaction.

3. How many constitutional isomers, $C_6H_{11}Cl$, can be formed in the free radical chlorination of methylcyclopentane (**1**)? What percentage of each structural isomer is formed? Write a radical chain reaction for the formation of the minor product. Calculate the heat of reaction for each propagation step and for the overall reaction with the minor isomer.



4. Cyclohexene (**1**) is expected to form only one constitutionally, isomeric monobromide. Why? What is its structure? On the other hand, compound **2**, 2-hexene, is expected to form four constitutional isomers based upon the reasoning applied to the bromination of **1**. Explain and illustrate.



5. Draw an energy diagram for the bromination of neopentane (2,2-dimethylpropane). Provide energies for each step and for the overall reaction, and clearly mark them in your diagram. Do justice to the Hammond Postulate.

6. Both CCl_4 and benzene (**1**) are effective solvents in the free radical bromination of cyclohexene (solute). Explain.

